

# Thermoelectric, thermionic and thermophotovoltaic energy conversion

Ali Shakouri  
Jack Baskin School of Engineering  
University of California Santa Cruz, CA 95064  
ali@soe.ucsc.edu

## Abstract

Key characteristics of thermoelectric, ballistic thermionic and quasi diffusive thermionic energy converters are compared. First, the main assumptions used to derive the linear Boltzmann transport equations for electrons are examined and the possibility that a higher order transport coefficient may become relevant is discussed. In the linear transport regime, there is a fundamental trade off between high Seebeck coefficient and high electrical conductivity for bulk materials and for many multilayer structures due to the interplay between electronic density-of-states (DOS) and electron group velocity and also due to the shape of DOS versus energy curve deep inside a band. While low dimensional structures alter the density-of-states, a similar trade off still exists. If large barrier heights and high doping concentrations could be achieved solid-state thermionic energy converters would be able to alleviate this trade off, thereby achieving a very high thermoelectric power factor. For this to occur, the electron transverse momentum perpendicular to heterostructure barriers must not be conserved. This can be achieved with non-planar structures or with embedded nanostructures. Finally, a comparison between thermoelectric/ thermionic devices and thermophotovoltaic energy converters shows a difference in the average energy of the emitted hot carriers due to the difference between electronic and photonic density-of-states in the reservoirs. The use of both electrons and photons from a hot reservoir or the engineering of the reservoir density-of-states may provide additional means to achieve higher efficiency in energy conversion devices and to approach the limit given by the entropy generation more easily.

## Linear/Nonlinear Transport Regime

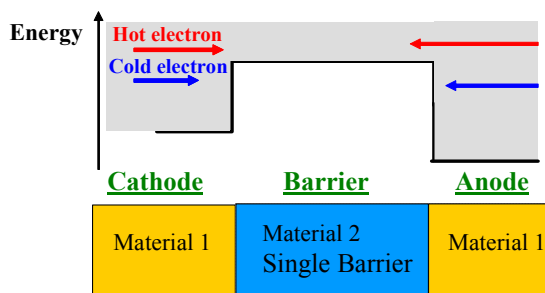
Conventional thermoelectric coolers and power generators operate in linear transport regime<sup>1</sup>. This means that the applied electric field and the temperature gradient slightly

perturb the electronic distribution function (the probability to find electrons at a given energy state and at a given location in the material). This is represented by a linear expansion of the perturbed distribution function as a function of electric field and temperature gradient. This gives rise to the conventional transport coefficients (electrical conductivity, electronic contribution to thermal conductivity and the Seebeck coefficient)<sup>2</sup>. Under the assumption that the local deviation from equilibrium is small, the Boltzmann transport equation can be linearized. Electrical and thermal currents can be thus written as:

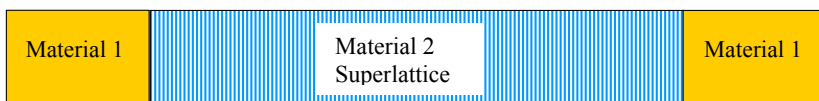
$$J(r) = \sigma \left( F - \frac{1}{q} \nabla E_f \right) + \sigma S (-\nabla T)$$

$$J_Q(r) = \sigma S T \left( F - \frac{1}{q} \nabla E_f \right) + \beta (-\nabla T),$$

where  $q$  is the unit charge of each carrier,  $T$  is the temperature,  $F$  is the local electric field, and  $E_f$  is the Fermi energy. The electrical conductivity  $\sigma$ , the Seebeck coefficient  $S$ , and the electronic thermal conductivity under zero electrochemical potential  $\beta$ , could be calculated using standard transport integrals which are various moments of the differential conductivity ( $\sigma(E)$ ). Differential conductivity represents the contribution of electrons of a given energy inside the material to the electron transport<sup>3,4</sup>. Differential conductivity depends on the density-of-states, momentum relaxation time and electron group velocity (see Fig. 3). Differential conductivity is non-zero only for electron energies within the Fermi window factor around the Fermi energy. This is due to the Pauli exclusion principle and the Fermion nature of electrons. The thermoelectric *figure-of-merit*  $ZT$  is defined as a function of the linear transport coefficients and it specifies how “good” the material is for thermoelectric cooling and power generation applications.



**Single Barrier Heterostructure Thermionic Energy Converter**



**Multibarrier/Superlattice Thermionic Energy Converter**

**Fig. 1** Band diagram of a single barrier heterostructure thermionic energy converter. Selective emission of hot electrons can produce electrical voltage under a temperature gradient. In the case of ballistic transport across the barrier, the device is in non-linear transport regime. If the barrier is made of a thick multibarrier or superlattice, under small biases, one can define an effective electrical conductivity and Seebeck coefficient by treating this as an effective medium.

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There are many electronic devices in which charge transport is non-linear and one has to go beyond the concept of electrical conductivity<sup>5</sup>. However non-linear thermoelectric effects have not been explored to a large extent. The thermoelectric effect at a pn junction is an example of where the bias-dependent Seebeck coefficient can be defined<sup>6</sup>. In the case of nanoscale heat and charge transport in superlattices, quantum wires and dots or in point contacts<sup>7</sup>, large temperature and electric field gradients and strong interaction of heat and electricity may require going to higher order terms in the above expansion of the distribution function. This will introduce novel transport coefficients, i.e. terms proportional to  $F^2$ ,  $\nabla T^2$ , etc. in equations (1) and (2). In this case, even the separation between electrical transport and thermoelectric transport may not be valid and one has to consider transport coefficients that are a function of both electric field and temperature gradient (terms proportional to  $F \cdot \nabla T$ ). A Monte Carlo simulation of the electron distribution function in a device under large electric fields and temperature gradients can give information on when these non-linear effects may be relevant.

### Single and Multibarrier Thermionic Devices

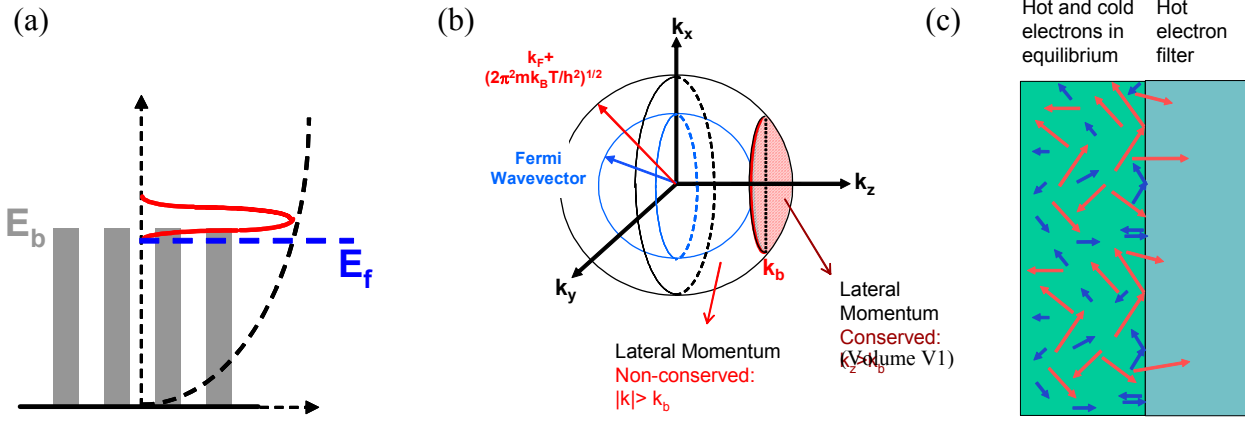
Heterostructure Integrated Thermionic (HIT) coolers have been made recently and characterized for applications in the integrated cooling of optoelectronic and electronic devices<sup>8,9,10,11</sup>. The idea of thermionic energy conversion was first seriously explored in the mid fifties during the development of vacuum diodes and triodes. Vacuum diode thermionic refrigerator was proposed by Mahan<sup>12</sup> in 1994. In early to mid nineties several groups pointed out the advantage of electron energy filters in bulk thermoelectric materials<sup>13,14,15</sup>. To overcome the limitations of vacuum thermionics at lower temperatures, thermionic emission cooling in heterostructures was proposed by Shakouri *et al.*<sup>8</sup> In these structures, a potential barrier is used for selective emission of hot electrons and evaporative cooling of the electron gas. The HIT cooler can be based on a single barrier or a multi barrier structure. In a single barrier structure in the ballistic transport regime, which is strongly nonlinear, electric current is dominated by the supply of electrons in the cathode layer and large cooling power densities can be achieved if optimum barrier height and thickness are chosen and if the anode is in contact with an ideal heat sink (see Fig. 1)<sup>9</sup>. However, the energy conversion efficiency in these structures is very low. Electrons that are ballistically emitted, release all their excess energy in the anode and produce significant heating.

On the other hand, for a multi barrier structure at small biases one can define an effective Seebeck coefficient and electrical conductivity (see Fig. 1)<sup>16,17</sup>. In the linear transport regime, calculations based on effective thermoelectrics material or based on solid-state thermionics will converge representing two points-of-views for the same electron transport phenomena in superlattices. One can describe the effect of potential barriers as a mean to increase the thermoelectric power factor (the square of the Seebeck coefficient times the electrical conductivity). The fact that there is a trade-off between electrical conductivity and the Seebeck coefficient and that we can not keep increasing the

number of free carriers and get higher and higher power factors is an intriguing effect which has not been discussed in detail from a fundamental point of view<sup>18,19,20</sup>. One way to look at this problem, is to consider the differential conductivity of electrons in typical semiconductors and metals. In a degenerate semiconductor, when the Fermi energy is close to the band edge (bottom of the conduction band or top of the valence band), the density-of-states versus energy curve is asymmetric with respect to the Fermi level. This means that there are more states available for transport above the Fermi energy than below it. As we increase the doping in the material, the Fermi energy moves deeper in the band and the differential conductivity becomes more symmetric with respect to the Fermi energy. This is due to the fact that the density-of-states has a square root dependence on energy for any typical 3D single band crystal. This can be explained by geometry considerations. Momentum is the main quantum number describing electrons in a crystal. Density-of-states is just a count of the number of electrons that occupy a given energy state. Since energy and momentum are related by a quadratic equation within the effective mass approximation, the number of states at a given energy scales as the surface area of the Fermi sphere in the momentum space. In 3D materials this surface (e.g. DOS) is proportional to the square root of the electron energy. Thus, it seems obvious that going to lower dimensional semiconductors can inherently improve the thermoelectric power factor by creating sharp features in electronic DOS. Sometimes it is mentioned that low dimensional structures have “increased” density-of-states. This is not strictly correct. Quantum confinement of electrons eliminate some states that electrons can occupy, since they don’t obey the boundary conditions for electronic wavefunction. Thus the number of available states (quantum numbers) associated with any given energy is either reduced or unchanged. The main benefit is that, near the bandedge, some sharp features in DOS are created. One can use these sharp features to increase the asymmetry between hot and cold electron transport and thus obtain a large thermoelectric power factor.

### Low-Dimensional Thermoelectrics

In 1993 the outstanding pioneering work of Hicks and Dresselhaus started a renewed interest in thermoelectrics, becoming the inspiration for most of the recent developments in the field<sup>21</sup>. Despite the fact that the concept of low-dimensional thermoelectrics is rigorously correct and proof-of-principle has been demonstrated<sup>22</sup>, it is interesting that the recent breakthroughs in materials with  $ZT > 1$  (Venkatasubramanian *et al.*<sup>23</sup>, Harman *et al.*<sup>24</sup>, or Kanatzidis *et al.*<sup>25</sup>) have mainly benefited from reduced phonon thermal conductivity<sup>26</sup> with power factors similar to the existing state-of-the-art material. There are two reasons why superlattice and nanowire materials using the concept of low dimensional thermoelectrics have not produced a high overall  $ZT$ . First, we live in a 3D world and any low dimensional quantum well or quantum wire structure should be imbedded in barriers which can reduce the performance significantly<sup>27,28</sup>. The second reason is that the sharp features in density-of-states of 2D and 1D nanostructures disappear quickly as soon as there is size non-uniformity in the material<sup>29</sup>.



**Fig. 2** (a) Schematic showing density-of-states in the conduction when the Fermi energy is deep in the band. Energy diagram of the multi barriers versus distance is superimposed to show the selective emission of hot electrons. (b) Representation of electronic states in momentum space when Fermi energy is deep inside a band (Fermi sphere). When lateral momentum is conserved, only electrons with large enough kinetic energy in the direction perpendicular to the barriers are transmitted (volume  $V_1$ ). However, when the lateral momentum is not conserved, number of emitted electrons increase substantially. (c) Diagrams of hot and cold electrons in real space. With planar barriers, hot electrons that are moving with large angle with respect to the interface are totally internally reflected.

Quantum dot structures have been proposed as the 0D extension of the low dimensional thermoelectrics<sup>24</sup>. However, there is a fundamental difference. The theory developed by Dresselhaus et al.<sup>21</sup> does not rigorously apply to quantum dots. The enhanced power factor in quantum confined 2D and 1D structures happens in the direction perpendicular to the confinement. Thus we benefit from sharp features in the density-of-states but we can still use free electron description with an effective mass in the direction where electric field is applied and heat is transported. However in the case of a matrix of quantum dots, electrons have to move between the dots in order to transfer heat from one location to another. If the electronic bands in the dots are very narrow, then electrons are highly confined and it is not easy to take them out of the dots. On the other hand, for shallow quantum dots it is easy to take electrons out but at the same time the density of electronic states in the dot will have broad features. As we will see in the next section, a significant benefit of quantum dots can be in hot electron filtering.

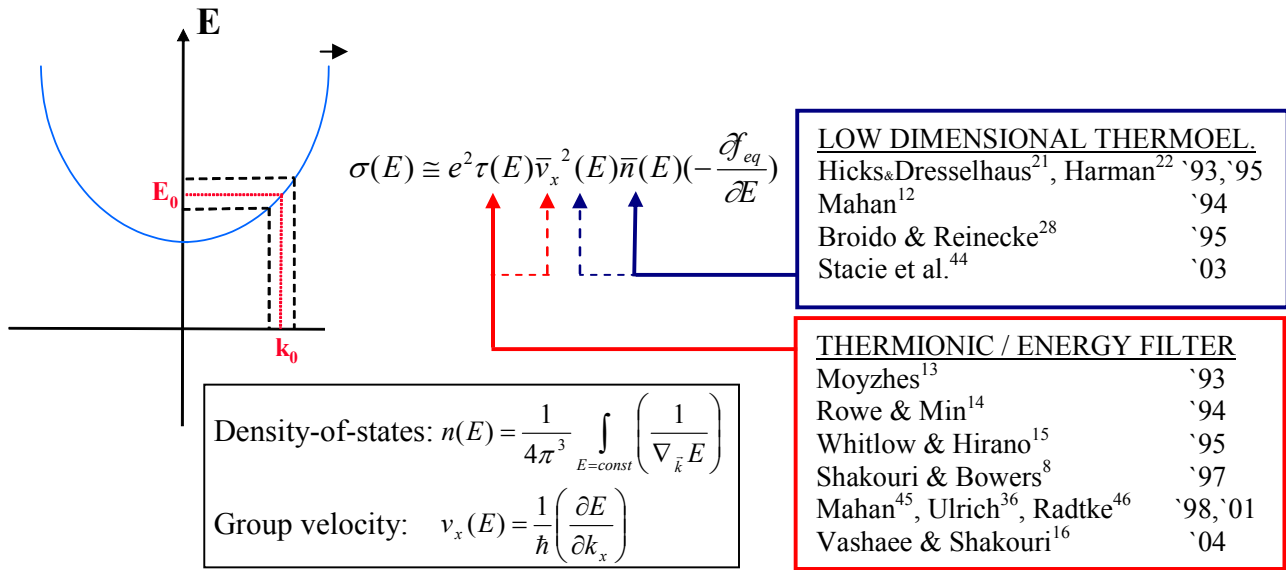
### Conservation of Transverse Momentum in Thermionic Emission

A judicious choice of potential barriers in a highly doped semiconductors or metals can increase the asymmetry between hot and cold electron transport, thereby overcoming the conventional trade-off between electrical conductivity and the Seebeck coefficient (see Fig. 2(a))<sup>30</sup>. However the simplistic picture in the energy space is misleading. One can think that all hot electrons with energies larger than the barrier height are transported above the barrier. However, if we look at electronic states in the momentum space (Fig. 2(b)), we see that with planar barriers, only electrons with kinetic energy in the direction perpendicular to the barrier higher than the threshold value are emitted (e.g. volume  $V_1$  in Fig. 2(b))<sup>16,17,19,31,32</sup>. There are many hot electrons that have large transverse momentum. They can not go above the barrier layer. In an analogy with optics, we can say that these

hot electrons have total internal reflection at the barrier interface and they can not be emitted (see Fig. 2(c)). The conservation of transverse momentum is due to the symmetry of the system (translation invariance in the direction perpendicular to the barrier layers). Using non-planar barriers or embedded nanostructures one can break this symmetry<sup>33</sup>. The key requirement is to break the symmetry without a significant reduction in the electron mean-free-path (electron mobility) in the structure. Thus it is important to have a low defect density and a high crystallinity near the interface. This could be achieved with e.g. embedded nanoparticles<sup>34</sup>. It is interesting to note that if there is transverse momentum conservation, not only the number of emitted electrons is reduced significantly, but also the energy filtering is not abrupt even with thick barriers<sup>35</sup>. Gradual selection of hot electrons results in low electronic efficiency of the structure.

### Electron Group Velocity and Electronic Density of States

Earlier, we discussed the inherent trade off between electrical conductivity and the Seebeck coefficient in solids. There is also a fundamental trade-off between electronic density-of-states and electron group velocity in crystalline solids<sup>30</sup>. This is manifested by the fact that solids with a high electron effective mass and/or multi valleys, have large densities of states, but at the same time they have lower mobilities. In Fig. 3 we can see that the electronic group velocity is related to the derivative of the dispersion relation (electron energy versus its momentum), while the density-of-states is related to the inverse of the band curvature<sup>2</sup>. Overall the shape of the density-of-states is dominating in thermoelectric and thermionic devices and materials with heavy electron masses and multiple valleys have large “material” figures-of-merit and good potentials for high  $ZT$ <sup>30,36,37</sup>. Low dimensional thermoelectrics and solid-state thermionics try to increase the asymmetry of the differential conductivity by modifying the density-of-states and the electron scattering, respectively. However one should



**Fig. 3** Electron dispersion relation for a simple parabolic band. Two important quantities in the expression of differential conductivity ( $\sigma(E)$ ), electronic density of states ( $n(E)$ ) and electron group velocity ( $v_x(E)$ ), can be directly calculated from the dispersion relation and they can not be changed independently. Recent research on low dimensional thermoelectrics and on solid-state thermionics (energy filtering) emphasizes the engineering of the differential conductivity by modifying density-of-states or by increasing cold electron relaxation ( $\tau(E)$ ). However they could also influence the electron group velocity as well.

remember that electron group velocity can also be modified and it is important that the overall product in the differential conductivity is optimized and not each term individually (see Fig. 3).

### Thermoelectric/Thermionic vs. Thermophotovoltaics

Thermophotovoltaics (TPV) is a competing technology for direct thermal to electric energy conversion. Thermal radiation from a hot source is incident to a filter that transmits only photons at the peak emission<sup>38</sup>. All other photons are reflected back to the hot source. Transmitted photons are converted to electron/hole pairs in a pn-junction diode. Significant losses in conventional photovoltaics<sup>39</sup> are avoided since the diode has a bandgap matching the peak emission of the hot source. TPV cells with efficiencies exceeding 20% have already been demonstrated<sup>40</sup>. They suffer from low power generation densities. Also, small bandgap bipolar diodes are very sensitive to non-radiative recombination in the depletion region, Auger recombination, etc. One of the reasons for which TPV cells have a higher efficiency than TE or solid-state TI devices is the fact that they have less parasitic losses. Heat conduction by phonons is a major loss mechanism since electrons are the ones that do the work, but in almost all practical thermoelectric material, the number of free electrons is several orders of magnitude less than the number of atoms undergoing vibrations and transmitting heat. Metal-based thermionic energy filters have the potential to overcome this problem and have much larger number of free electrons participating in the transport. However, there is another fundamental limit. As it was pointed out in a lucid paper by Humphrey and Linde<sup>41</sup>, there are inherent electronic thermal conduction losses since electrons are in contact with both hot and cold reservoirs. If the electronic band in the material has a finite width, there is some heat transfer

between the two reservoirs even when there is no net voltage generated. Electrons with energies less than the Fermi energy move from the cold side to the hot one, while electrons with energies higher than the Fermi move from the hot contact to the cold one. There is no net current, but there is entropy generation<sup>42</sup>. This problem can be overcome if the material is designed in a way that there is monoenergetic electron transport at a special energy level. This is analogous to the photon filter in TPV devices that transmit only “good” photons. Another interesting difference between TE/TI devices and TPV devices is the fact that the average energy of photons exchanged between hot and cold reservoirs is higher than the average energy of electrons exchanged with reservoirs at the same temperature (see Fig. 4). The peak in the Planck distribution at e.g. 900K is photons with energies of  $\sim 0.4\text{eV}$  while the electron average energy is  $\sim 3 \times 0.075 = 0.22\text{eV}$  (assuming 3 degrees of freedom). This may seem curious since the same Carnot limit applies to both electrons and photons. Carnot efficiency is not derived for specific distribution functions and it is based on general thermodynamic arguments<sup>43</sup>. It seems that working with different energy carriers (electrons, photons, etc.) and with reservoirs with different internal degrees of freedom may provide another opportunity to engineer the efficiency of the heat engines and to approach the entropy limit (2<sup>nd</sup> law of thermodynamics) more easily.

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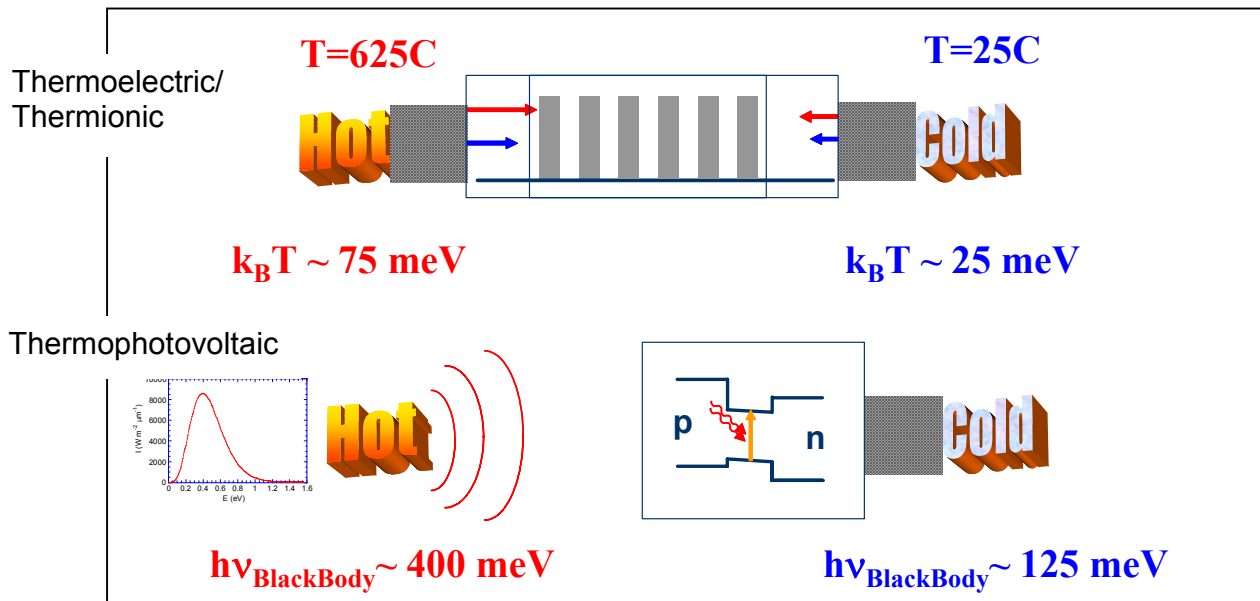


Figure 4

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